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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

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Takeo WATANABE, et al.

JUL 5 - 2002

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Group Art Unit: 2344

TC 1700

Confirmation No.: 1880

Examiner: NOT YET ASSIGNED

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For: POLYMERIZABLE COMPOSITION, CURED MATERIAL THEREOF AND METHOD
FOR MANUFACTURING THE SAME

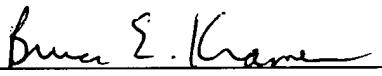
SUBMISSION OF SWORDN TRANSLATION OF PROVISIONAL APPLICATION

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Pursuant to 37 C.F.R. §1.78(a)(5), submitted herewith is a sworn English language
translation of Provisional Application No. 60/263,163, upon which a claim for benefit is based.

Respectfully submitted,


Bruce E. Kramer
Registration No. 33,725

SUGHRUE MION, PLLC
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037-3213
Telephone: (202) 293-7060
Facsimile: (202) 293-7860
Date: June 26, 2002

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DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/263,163 filed on January 23, 2001.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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Signed this 29th day of March, 2001

JUL 5 - 2002

TC 1700

Atsuko Ikeda
Atsuko Ikeda

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[NAME OF DOCUMENT] Specification

TC 1700

[TITLE OF THE INVENTION]

Polymerizable Composition, Cured Material Thereof and
Method for Manufacturing the Same

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat.

[Claim 2] The polymerizable composition as claimed in claim 1, wherein the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat is a compound capable of generating an acid under irradiation of an active energy ray and/or under heat and thereby initiating the cationic polymerization.

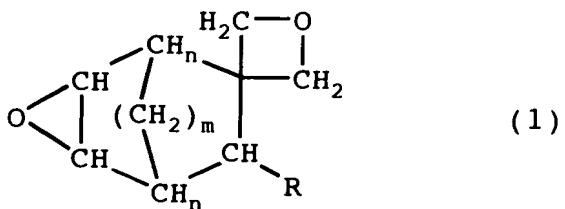
[Claim 3] The polymerizable composition as claimed in claim 1 or 2, wherein the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat is one or more compound selected from sulfonium salts, iodonium salts and diazonium salts.

[Claim 4] The polymerizable composition as claimed in any one of claims 1 to 3, wherein the alicyclic alkane

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(a) having an oxetanyl group and an epoxy group within the same molecule is a compound represented by formula (1):

[Chem. 1]



(1)

(wherein R represents a hydrogen atom or a methyl group, m represents an integer of 0 to 2, n is 2 when m is 0 and otherwise n is 1).

[Claim 5] The polymerizable composition as claimed in any one of claims 1 to 4, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane.

[Claim 6] The polymerizable composition as claimed in any one of claims 1 to 5, which comprises a compound (c) that can be cationic polymerized by the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat, and that is not the compound (a).

[Claim 7] The polymerizable composition as claimed in claim 6, wherein at least one compound (c) is a compound (c-1) having one or more epoxy group.

[Claim 8] The polymerizable composition as claimed in claim 6, wherein at least one compound (c) is a compound (c-2) having one or more oxetanyl group.

[Claim 9] The polymerizable composition as claimed in any one of claims 1 to 8, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is blended in an amount of 5 to 100 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[Claim 10] The polymerizable composition as claimed in claim 7 or 9, wherein the compound (c-1) having one or more epoxy group is blended in an amount of 5 to 95 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[Claim 11] The polymerizable composition as claimed in claim 8 or 9, wherein the compound (c-2) having one or more oxetanyl group is blended in an amount of 5 to 95 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[Claim 12] A cured material obtained by polymerizing

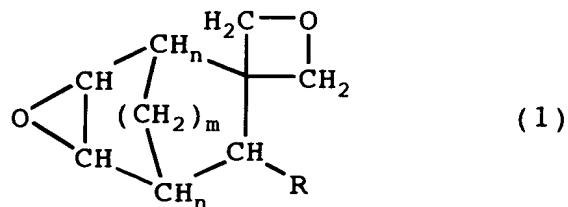
a polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat.

[Claim 13] The cured material as claimed in claim 12, wherein the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat is a compound capable of generating an acid under irradiation of an active energy ray and/or under heat and thereby initiating the cationic polymerization.

[Claim 14] The cured material as claimed in claim 12 or 13, wherein the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat is one or more compound selected from sulfonium salts, iodonium salts and diazonium salts.

[Claim 15] The cured material as claimed in any one of claims 12 to 14, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is a compound represented by formula (1):

[Chem. 2]



(wherein R represents a hydrogen atom or a methyl group, m represents an integer of 0 to 2, n is 2 when m is 0 and otherwise n is 1).

[Claim 16] The cured material as claimed in any one of claims 12 to 15, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane.

[Claim 17] The cured material as claimed in any one of claims 12 to 16, which comprises a compound (c) that can be cationic polymerized by the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat, and that is not the compound (a).

[Claim 18] The cured material as claimed in claim 17, wherein at least one compound (c) is a compound (c-1) having one or more epoxy group.

[Claim 19] The cured material as claimed in claim 17, wherein at least one compound (c) is a compound (c-2) having one or more oxetanyl group.

[Claim 20] The cured material as claimed in any one of claims 12 to 19, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is blended in an amount of 5 to 100 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization

under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[Claim 21] The cured material as claimed in claim 18 or 20, wherein the compound (c-1) having one or more epoxy group is blended in an amount of 5 to 95 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of polymerizable composition.

[Claim 22] The cured material as claimed in any one of claims 19 to 21, wherein the compound (c-2) having one or more oxetanyl group is blended in an amount of 5 to 95 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[Claim 23] A method for manufacturing a cured material obtained from a polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat, said method comprising initiating the polymerization under irradiation of an active energy ray and/or under heat.

[Claim 24] A method for manufacturing a cured material described in any one of claims 12 to 22, comprising initiating the polymerization under irradiation of an active energy ray.

[Claim 25] A method for manufacturing a cured material described in any one of claims 12 to 22, comprising initiating the polymerization under heat.

[Claim 26] A method for manufacturing a cured material described in any one of claims 12 to 22, comprising initiating the polymerization under irradiation of an active energy ray and then heating the composition.

[Claim 27] The method for manufacturing a cured material as claimed in claim 24 or 26, wherein the active energy ray is an ultraviolet ray.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a polymerizable composition which quickly polymerizes under irradiation of an active energy ray such as ultraviolet ray or electron beam and/or under heat to provide a cured material, a method for polymerizing the composition and a cured material obtained by polymerizing the composition.

[0002]

[Background Art]

Curing of a resin by an active energy ray such as ultraviolet ray is favored with various characteristics, for example, high curing rate and good workability without solvent are ensured and the necessary energy amount is very small, therefore, this technique is playing a very important role in various fields such as wood coating, metal painting and printing. At the initial stage of development in these fields, studies are exclusively directed to ultraviolet ray initiation radical polymerization of a polyfunctional acrylate, an unsaturated polyester or the like, and various materials comprising a polyfunctional acrylate, an unsaturated polyester or the like have been heretofore used. Even at the present time, most of studies are directed to ultraviolet ray initiation radical polymerization, however, it is now recognized that photoinitiation ionic polymerization is also fairly promising in various applied fields. The photoinitiation ionic polymerization, in which various monomers can be used, has a possibility of providing cured materials having various chemical and physical properties and therefore, this technique is attracting an attention.

[0003]

The photocationic polymerizable composition is

constructed by a photocationic polymerization initiator (photoacid generator) capable of decomposing under irradiation of an active energy ray such as ultraviolet ray and generating an acid, and a compound capable of causing a polymerization reaction or a crosslinking reaction by the acid generated. The development thereof is exclusively directed to an epoxy resin having oxirane ring which is a 3-membered cyclic ether, and the photocurable epoxy resin is known to have excellent properties in the adhesion, heat resistance and chemicals resistance. However, conventional photocurable epoxy resins have a problem in that the photocuring rate is very low. Therefore, it has been keenly demanded to improve the curing rate while maintaining the properties of the epoxy resin.

[0004]

The polyfunctional oxetane monomer contains a plurality of oxetane rings which are a four-membered ring cyclic ether, as the polymerizable group within one molecule and is reported to have photocurability equal to or higher than that of the corresponding polyfunctional epoxide (see, Journal of Macromolecular Science, Vol. A 29, No. 10, page 915 (1992); ibid., Vol. 30, Nos. 2 & 3, page 173; ibid., Vol. 30, Nos. 2 & 3, page 189 (1993)). Also, a photocurable composition mainly comprising a polyfunctional oxetane monomer has been proposed (see, JP-A-6-16804 (the

term "JP-A" as used herein means an "unexamined published Japanese patent application"). The ultraviolet ray curable resin using this polyfunctional oxetane monomer shows a high curing rate under irradiation of an ultraviolet ray as compared with epoxy resin, however, encounters difficulties in the application to uses as in the coating on a material having low heat resistance, such as paper or plastic. Also, a higher photocuring rate is demanded.

[0005]

The photocationic polymerization curable epoxy resin composition or photocationic polymerization curable oxetane compound-containing resin composition may also be thermopolymerized by adding a heat cationic polymerization initiator which decomposes under heat to generate an acid, in place of adding a photocationic polymerization initiator. The photocationic polymerization initiator accelerates the ring-opening cationic polymerization of a cationic polymerizable compound under irradiation of an active energy ray. On the other hand, the heat cationic polymerization initiator accelerates the ring-opening cationic polymerization when the compound is heated from outside or left standing at room temperature and this is a particularly important technique in the field where the photocationic polymerization cannot be performed, for example, in the curing of a material having poor light

transmittance or in the manufacture of a thick cast molded article. The heat cationic polymerization is described in JP-A-11-246541, JP-A-11-106380 and JP-A-11-61034. However, similarly to the photocationic polymerization, the heat cationic polymerization curable epoxy resin composition, the heat cationic polymerization curable oxetane compound-containing resin composition and a mixture thereof are not sufficiently high in the curing rate and for obtaining a cured material, a high temperature treatment for a long period of time is necessary or a large amount of heat cationic polymerization initiator is required. A composition satisfying productivity and profitability has not yet been obtained.

[0006]

U.S. Patent 3,388,105 describes a technique of curing an alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule by addition-reacting it under heat with a carboxyl group-containing compound, however, it is not known that this alicyclic alkane exhibits very high activity (curability) in the cationic ring-opening polymerization.

[0007]

[Problems to be Solved by the Invention]

Under these circumstances, the present invention has been made and the object of the present invention is to

provide a cationic polymerizable composition capable of exhibiting high activity (quick polymerizability, quick curability) under irradiation of an active energy ray and/or under heat.

[0008]

[Means to Solve the Problems]

As a result of extensive investigations to solve the above-described problems, the present inventors have found that a polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat exhibits high activity (quick polymerizability, quick curability) in the cationic ring-opening polymerization under irradiation of an active energy ray and/or under heat and at the same time, found that the polymerization product thereof (cured material) has good properties. The present invention has been accomplished based on these findings.

[0009]

More specifically, the present invention relates to a polymerizable composition, a cured material obtained by polymerizing the composition and a method for manufacturing the cured material, described in the followings (1) to (27).

[0010]

(1) A polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat.

[0011]

(2) The polymerizable composition as described in (1) above, wherein the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat is a compound capable of generating an acid under irradiation of an active energy ray and/or under heat and thereby initiating the cationic polymerization.

[0012]

(3) The polymerizable composition as described in (1) or (2) above, wherein the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat is one or more compound selected from sulfonium salts, iodonium salts and diazonium salts.

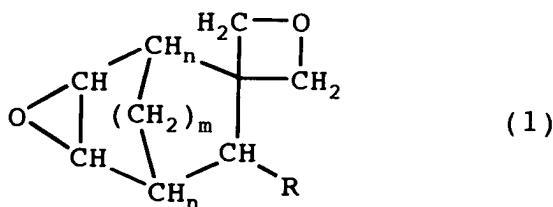
[0013]

(4) The polymerizable composition as described in any one of (1) to (3) above, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same

molecule is a compound represented by formula (1):

[0014]

[Chem. 3]



(wherein R represents a hydrogen atom or a methyl group, m represents an integer of 0 to 2, n is 2 when m is 0 and otherwise n is 1).

[0015]

(5) The polymerizable composition as described in any one of (1) to (4) above, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane.

[0016]

(6) The polymerizable composition as described in any one of (1) to (5) above, which comprises a compound (c) that can be cationic polymerized by the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat, and that is not the compound (a).

[0017]

(7) The polymerizable composition as described in (6) above, wherein at least one compound (c) is a compound (c-1) having one or more epoxy group.

[0018]

(8) The polymerizable composition as described in (6) above, wherein at least one compound (c) is a compound (c-2) having one or more oxetanyl group.

[0019]

(9) The polymerizable composition as described in any one of (1) to (8) above, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is blended in an amount of 5 to 100 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[0020]

(10) The polymerizable composition as described in (7) or (9) above, wherein the compound (c-1) having one or more epoxy group is blended in an amount of 5 to 95 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[0021]

(11) The polymerizable composition as described in (8) or (9) above, wherein the compound (c-2) having one or more oxetanyl group is blended in an amount of 5 to 95 wt% based

on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[0022]

(12) A cured material obtained by polymerizing a polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat.

[0023]

(13) The cured material as described in (12) above, wherein the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat is a compound capable of generating an acid under irradiation of an active energy ray and/or under heat and thereby initiating the cationic polymerization.

[0024]

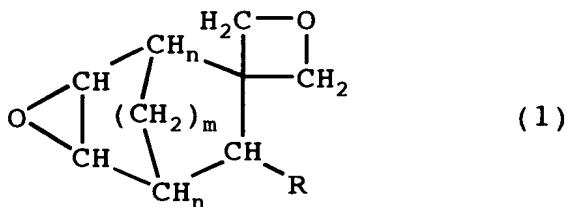
(14) The cured material as described in (12) or (13) above, wherein the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat is one or more compound selected from sulfonium salts, iodonium salts and diazonium salts.

[0025]

(15) The cured material as described in any one of (12) to (14) above, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is a compound represented by formula (1):

[0026]

[Chem. 4]



(wherein R represents a hydrogen atom or a methyl group, m represents an integer of 0 to 2, n is 2 when m is 0 and otherwise n is 1).

[0027]

(16) The cured material as described in any one of (12) to (15) above, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane.

[0028]

(17) The cured material as described in any one of (12) to (16) above, which comprises a compound (c) that can be cationic polymerized by the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat, and that is not the compound (a).

[0029]

(18) The cured material as described in (17) above, wherein at least one compound (c) is a compound (c-1) having one or more epoxy group.

[0030]

(19) The cured material as described in (17) above, wherein at least one compound (c) is a compound (c-2) having one or more oxetanyl group.

[0031]

(20) The cured material as described in any one of (12) to (19) above, wherein the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule is blended in an amount of 5 to 100 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[0032]

(21) The cured material as described in (18) or (20) above, wherein the compound (c-1) having one or more epoxy group is blended in an amount of 5 to 95 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of polymerizable composition.

[0033]

(22) The cured material as described in any one of (19) to (21) above, wherein the compound (c-2) having one or more oxetanyl group is blended in an amount of 5 to 95 wt% based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition.

[0034]

(23) A method for manufacturing a cured material obtained from a polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat, the method comprising initiating the polymerization under irradiation of an active energy ray and/or under heat.

[0035]

(24) A method for manufacturing a cured material described in any one of (12) to (22) above, comprising initiating the polymerization under irradiation of an active energy ray.

[0036]

(25) A method for manufacturing a cured material

described in any one of (12) to (22) above, comprising initiating the polymerization under heat.

[0037]

(26) A method for manufacturing a cured material described in any one of (12) to (22) above, comprising initiating the polymerization under irradiation of an active energy ray and then heating the composition.

[0038]

(27) The method for manufacturing a cured material as described in (24) or (26) above, wherein the active energy ray is an ultraviolet ray.

[0039]

[Mode for Carrying Out the Invention]

The present invention is described in detail below.

[0040]

The present invention relates to a polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat, and also relates to a method for polymerizing the composition and a cured material of the composition.

[0041]

Examples of the alicyclic alkane (a) having an

oxetanyl group and an epoxy group within the same molecule for use in the present invention include 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane, 6,7-epoxy-2-oxa-[3.5]spirononane, 7,8-epoxy-2-oxa-5-methyl-[3.6]spirodecane, 5,6-epoxy-2-oxa-[3.6]spirodecane, spiro[5,6-epoxynorbornane-2,3'-oxatane] and spiro[5,6-epoxy-3-methylnorbornane-2,3'-oxetane]. Among these, preferred are 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane, 6,7-epoxy-2-oxa-[3.5]spirononane and spiro[5,6-epoxynorbornane-2,3'-oxetane].

[0042]

These alicyclic alkanes having an oxetanyl group and an epoxy group within the same molecule can be easily synthesized by a known method described, for example, in U.S. Patent 3,388,105.

[0043]

These alicyclic alkanes (a) having an oxetanyl group and an epoxy group within the same molecule can be used individually or as a mixture of two or more thereof.

[0044]

The compound (a) is suitably blended in an amount of from 5 to 100 wt% (in the case of using two or more compounds (a) in combination, the total amount thereof) based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray

and/or under heat from the total weight of the polymerizable composition of the present invention.

[0045]

The compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat for use in the present invention may be a compound which changes under heat or under irradiation of an active energy ray such as ultraviolet ray and thereby generates a substance capable of initiating the cationic polymerization, such as an acid. Accordingly, the compound (b) is a kind of cationic polymerization initiator and called an "acid generator" in the art. In the present invention, the compound (b) is hereinafter referred to as an acid generation-type cationic polymerization initiator.

[0046]

The acid generation-type cationic polymerization initiator is blended for the purpose of accelerating the ring-opening cationic polymerization of both the oxetanyl group and the epoxy group in the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule of the present invention, under heat or irradiation of light such as ultraviolet ray, and allowing the curing to proceed smoothly to form a cured material or paint film.

[0047]

The acid generation-type cationic polymerization initiator as used in the present invention is a compound which changes under heat or under irradiation of an active energy ray such as ultraviolet ray and thereby generates a substance capable of initiating the cationic polymerization, such as an acid, and compounds taking the form of an acid from the beginning, such as carboxylic acid, are excluded.

[0048]

Examples of the acid generation-type cationic polymerization initiator include known sulfonium salts, iodonium salts, phosphonium salts, diazonium salts, ammonium salts, ferrocenes and the like. Specific examples thereof are described below, however, the present invention is not limited to these compounds.

[0049]

Examples of the sulfonium salt-based acid generation-type cationic polymerization initiator include bis[4-(diphenylsulfonio)phenyl]sulfide bishexafluorophosphate, bis[4-(diphenylsulfonio)phenyl]sulfide bishexafluoro-antimonate, bis[4-(diphenylsulfonio)phenyl]sulfide bistetrafluoroborate, bis[4-(diphenylsulfonio)phenyl]-sulfide tetrakis(pentafluorophenyl)borate, diphenyl-4-(phenylthio)phenylsulfonium hexafluorophosphate, diphenyl-4-(phenylthio)phenylsulfonium hexafluoroantimonate,

diphenyl-4-(phenylthio)phenylsulfonium tetrafluoroborate,
diphenyl-4-(phenylthio)phenylsulfonium tetrakis(penta-
fluorophenyl)borate, triphenylsulfonium hexafluorophosphate,
triphenylsulfonium hexafluoroantimonate, triphenylsulfonium
tetrafluoroborate, triphenylsulfonium tetrakis(pentafluoro-
phenyl)borate, bis[4-(di(4-(2-hydroxyethoxy)phenyl-
sulfonio)phenyl]sulfide bishexafluorophosphate, bis[4-
(di(4-(2-hydroxyethoxy)phenylsulfonio)phenyl]sulfide bis-
hexafluoroantimonate, bis[4-(di(4-(2-hydroxyethoxy))-
phenylsulfonio)phenyl]sulfide bistetrafluoroborate and
bis[4-(di(4-(2-hydroxyethoxy)phenylsulfonio)phenyl]sulfide
tetrakis(pentafluorophenyl)borate.

[0050]

Examples of the iodonium salt-based acid generation-type cationic polymerization initiator include diphenyl-iodonium hexafluorophosphate, diphenyliodonium hexafluoroantimonate, diphenyliodonium tetrafluoroborate, diphenyliodonium tetrakis(pentafluorophenyl)borate, bis(dodecylphenyl)iodonium hexafluorophosphate, bis(dodecylphenyl)iodonium hexafluoroantimonate, bis(dodecylphenyl)-iodonium tetrafluoroborate, bis(dodecylphenyl)iodonium tetrakis(pentafluorophenyl)borate, 4-methylphenyl-4-(1-methylethyl)phenyliodonium hexafluorophosphate, 4-methylphenyl-4-(1-methylethyl)phenyliodonium hexafluoroantimonate, 4-methylphenyl-4-(1-methylethyl)phenyliodonium

tetrafluoroborate and 4-methylphenyl-4-(1-methylethyl)-phenyliodonium tetrakis(pentafluorophenyl)borate.

[0051]

Examples of the diazonium salt-based acid generation-type cationic polymerization initiator include phenyldiazonium hexafluorophosphate, phenyldiazonium hexafluoroantimonate, phenyldiazonium tetrafluoroborate and phenyldiazonium tetrakis(pentafluorophenyl)borate.

[0052]

Examples of the ammonium salt-type acid generation-type cationic polymerization initiator include 1-benzyl-2-cyanopyridinium hexafluorophosphate, 1-benzyl-2-cyano-pyridinium hexafluoroantimonate, 1-benzyl-2-cyanopyridinium tetrafluoroborate, 1-benzyl-2-cyanopyridinium tetrakis(pentafluorophenyl)borate, 1-(naphthylmethyl)-2-cyano-pyridinium hexafluorophosphate, 1-(naphthylmethyl)-2-cyanopyridinium hexafluoroantimonate, 1-(naphthylmethyl)-2-cyanopyridinium tetrafluoroborate and 1-(naphthylmethyl)-2-cyanopyridinium tetrakis(pentafluorophenyl)borate.

[0053]

Examples of the ferrocene-based acid generation-type cationic polymerization initiator include (2,4-cyclopentadien-1-yl)[(1-methylethyl)benzene]-Fe(II) hexafluorophosphate, (2,4-cyclopentadien-1-yl)[(1-methylethyl)benzene]-Fe(II) hexafluoroantimonate, (2,4-cyclopentadien-

1-yl)[(1-methylethyl)benzene-Fe(II) tetrafluoroborate and (2,4-cyclopentadien-1-yl)[(1-methylethyl)benzene]-Fe(II) tetrakis(pentafluorophenyl)borate.

[0054]

Among these, sulfonium salt-based and iodonium salt-based acid generation-type cationic polymerization initiators are preferred in view of curing rate, stability and profitability. Examples of the commercially available product include SP-150, SP-170, CP-66 and CP-77 produced by Asahi Denka Kogyo; CYRACURE-UVI-6990 and UVI-6974 produced by Union Carbide; CI-2855 and CI-2639 produced by Nippon Soda; San-Aid SI-60 produced by Sanshin Kagaku Kogyo K.K.; IRGACURE 261 ((2,4-cyclopentadien-1-yl)[(1-methylethyl)benzene]-Fe(II) hexafluorophosphate) produced by Ciba Specialty Chemicals; and RHODORSIL 2074 (4-methylphenyl-4-(1-methylethyl)phenyliodonium tetrakis(pentafluorophenyl)borate) produced by Rhone Puran.

[0055]

The acid generation-type cationic polymerization initiator may be selected from the above-described materials and these materials may be used individually or in combination of two or more thereof. The acid generation-type cationic polymerization initiator is not particularly limited on the suitable range of the amount used but is preferably used in an amount of 0.05 to 25 parts by mass,

preferably from 1 to 10 parts by mass, based on the total amount (100 parts by mass) of the polymerizable compounds (namely, the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the same molecule and the compound (c)) which can be cationic polymerized by the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat. If the amount added is less than 0.05 parts by mass, poor sensitivity results and a tremendously large light irradiation energy or a high-temperature treatment for a long time period is necessary for the curing. On the other hand, even if the amount added exceeds 25 parts by mass, the sensitivity does not increase and this is not preferred also in view of the profitability, moreover, the amount of the initiator remaining in the paint film as an uncured component increases and the physical properties of the cured product may deteriorate.

[0056]

For the compound (c-1) having an epoxy group for use in the present invention, an epoxy compound commonly known and used can be used and the compound is not particularly limited as long as it has one or more epoxy group within one molecule.

[0057]

Specific examples of the compound which can be used

include bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl ether, brominated bisphenol A diglycidyl ether, brominated bisphenol F diglycidyl ether, brominated bisphenol S diglycidyl ether, epoxy novolak resin, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, hydrogenated bisphenol S diglycidyl ether, cresol novolak epoxy resin and triglycidyl isocyanurate.

[0058]

Examples of the alicyclic epoxy compound include (3,4-epoxycyclohexyl)methyl-3',4'-epoxycyclohexyl carboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-meta-dioxane, bis(3,4-epoxycyclohexylmethyl) adipate, vinylcyclohexene oxide, 4-vinylepoxyhexane, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, 3,4-epoxy-6-methylcyclohexyl-3',4'-epoxy-6'-methylcyclohexane carboxylate, methylenebis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, di(3,4-epoxycyclohexylmethyl) ether of ethylene glycol, and ethylenebis(3,4-epoxycyclohexane carboxylate).

[0059]

Other examples include polyglycidyl ethers of a polyether polyol obtained by adding one or more alkylene oxide to an aliphatic polyhydric alcohol, such as dioctyl epoxyhexahydrophthalate, di-2-ethylhexyl epoxyhexahydro-

phthalate, 1,4-butanedioldiglycidyl ether, 1,6-hexanediol-diglycidyl ether, glycerol triglycidyl ether, trimethylol-propane triglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, ethylene glycol, propylene glycol and glycerol; diglycidyl ethers of aliphatic long-chained dibasic acid; monoglycidyl ethers of aliphatic higher alcohol; butyl glycidyl ether, phenyl glycidyl ether, cresol glycidyl ether, nonylphenyl glycidyl ether, glycidyl methacrylate; monoglycidyl ethers of phenol, cresol, butylphenol or polyether alcohol obtained by adding an alkylene oxide thereto; glycidyl esters of higher fatty acid; epoxidated soybean oil; butyl epoxystearate, octyl epoxystearate, epoxidated linseed oil and epoxidated polybutadiene.

[0060]

These compounds (c-1) having one or more epoxy group within the molecule can be used individually or as a mixture of two or more thereof.

[0061]

The compound (c-1) can be blended in an amount of 5 to 95 wt% (in the case of using two or more compounds (c-1) in combination, the total amount thereof) based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from

the total weight of the polymerizable composition of the present invention.

[0062]

The compound (c-2) having one or more oxetanyl group within the molecule is described below. The compound (c-2) having one or more oxetanyl group is used for the purpose of adjusting the viscosity of the polymerizable composition as a whole according to the use end and also imparting an effect considered ascribable to the oxetane compound, namely, water resistance or reduction in the curing shrinkage.

[0063]

Specific examples thereof include trimethylene oxide, 3,3-dimethyloxetane, 3,3-bischloromethyloxetane, 3-ethyl-3-phenoxy methyloxetane, 3-ethyl-3-hydroxymethyloxetane (EOXA, trade name, produced by Toa Gosei), bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene (also called xylylene dioxetane; XDO, trade name, produced by Toa Gosei), tri[(3-ethyl-3-oxetanylmethoxy)methyl]benzene, bis[(3-ethyl-3-oxetanylmethoxy)methylphenyl]ether, (3-ethyl-3-oxetanylmethoxy)oligodimethylsiloxane, and compounds containing a plurality of oxetane rings having a high molecular weight, specifically, oxetane oligomer (Oligo-OXT, trade name, produced by Toa Gosei)

[0064]

Examples of the compound having an alicyclic structure other than an oxetane ring within the same compound include 2-oxaspiro[3.5]nonane, 7-methyl-2-oxaspiro[3.5]nonane, spiro[adamantane-2,3'-oxetane], spiro[bicyclo[2.2.1]-heptane-2,3'-oxetane], spiro[bicyclo[2.2.2]octane-2,3'-oxetane], spiro[7-oxabicyclo[2.2.1]heptane-2,3'-oxetane], 2-oxaspiro[3.5]non-6-ene, 5-methyl-2-oxaspiro[3.5]non-6-ene, spiro[bicyclo[2.2.1]hept-5-ene-2,3'-oxetane], spiro[3-methylbicyclo[2.2.1]hept-5-ene-2,3'-oxetane], 5-methyl-2-oxaspiro[3.5]nonane and spiro[3-methylbicyclo[2.2.1]-heptane-2,3'-oxetane].

[0065]

These compounds (c-2) having one or more oxetanyl group can be used individually or as a mixture of two or more thereof.

[0066]

The compound (c-2) can be blended in an amount of 5 to 95 wt% (in the case of using two or more compounds (c-2) in combination, the total amount thereof) based on the weight obtained by subtracting the weight of the compound (b) capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat from the total weight of the polymerizable composition of the present invention.

[0067]

In the present invention, a cationic polymerizable monomer described below can also be added to the polymerizable composition. This cationic polymerizable monomer is classified into a compound which is the compound (c) that causes a polymerization reaction or crosslinking reaction by the acid generated from the acid generation-type cationic polymerization initiator, but which is not the compound (c-1) or (c-2). Examples thereof include oxolane compounds such as tetrahydrofuran, 2,3-dimethyltetrahydrofuran; cyclic acetal compounds such as trioxan, 1,3-dioxolane and 1,3,6-trioxancyclooctane; cyclic lactone compounds such as β -propiolactone and ϵ -caprolactone; thiirane compounds such as ethylenesulfide, 1,2-propylenesulfide and thioepichlorohydrin; thiethane compounds such as 3,3-dimethylthiethane; vinyl ether compounds such as ethylene glycol divinyl ether, triethylene glycol divinyl ether, trimethylol propane trivinyl ether; spiroorthoester compounds as a reaction product of an epoxy compound with lactone; ethylenically unsaturated compounds such as vinylcyclohexane, isobutylene and polybutadiene; cyclic ether compounds; cyclic thioether compounds; and vinyl compounds.

[0068]

These cationic polymerizable monomers can be added

individually or in combination of two or more thereof.

[0069]

In polymerizing the polymerizable composition of the present invention by an ultraviolet ray which is one of active energy rays, a sensitizer may also be used for improving the polymerization rate. Examples of the sensitizer used to this purpose include pyrene, perylene, 2,4-diethylthioxanthone, 2,4-dimethylthioxanthone, 2,4-dichlorothioxanthone and phenothiazine. In the case of using a sensitizer in combination, the sensitizer is preferably used in an amount of 0.1 to 100 parts by mass per 100 parts by mass of photoacid generation-type cationic polymerization initiator.

[0070]

The polymerizable composition of the present invention may also contain an organic solvent. The organic solvent is used for the purpose of adjusting the viscosity according to the use or the coating method or in the case where the polymerizable composition is solid, for dissolving and diluting the polymerizable composition and thereby enabling the coating of the polymerizable composition in the liquid form. Specific examples of the organic solvent which can be used include known solvents such as acetone, hexane, ethyl acetate, diethyl ether, ethyl methyl ketone, cyclohexane, tetrahydrofuran, toluene, xylene, tetramethylbenzene,

petroleum ether, petroleum naphtha and solvent naphtha; ethylene glycol monoalkyl ethers and acetates thereof; diethylene glycol mono- or di-alkyl ethers; propylene glycol monoalkyl ethers and acetates thereof; dipropylene glycol mono- or di-alkyl ethers; methyl carbitol, butyl carbitol, butyl cellosolve acetate and carbitol acetate.

[0071]

These organic solvents can be used individually or in combination of two or more thereof. The amount of this organic solvent used can be appropriately selected according to the use end or the coating method.

[0072]

In the case of applying the polymerizable composition of the present invention to uses where adhesion, hardness or the like is required, a commonly known inorganic filler may be used, if desired, for the purpose of improving various properties and examples thereof include barium sulfate, barium titanate, powdered silicon oxide, finely powdered silicon oxide, amorphous silica, talc, clay, magnesium carbonate, calcium carbonate, aluminum oxide, aluminum hydroxide and mica powder. Furthermore, if desired, commonly known additives may also be added and examples thereof include a coloring agent such as Phthalocyanine Blue, Phthalocyanine Green, Iodine Green, Disazo Yellow, Crystal Violet, titanium oxide, carbon black and

naphthalene black; a silicone-type, fluorine-type or polymer-type defoaming agent and/or leveling agent; and an adhesion-imparting agent such as imidazole type, thiazole type, triazole type or silane coupling agent.

[0073]

Polymerization Method of Polymerizable Composition of the Present Invention:

The polymerizable composition of the present invention can be polymerized (cured) under irradiation of an active energy ray and/or under heat. The term "active energy ray" as used herein means an ultraviolet ray, an X ray, an electron beam, a γ ray or the like. In the case of irradiating an ultraviolet ray, examples of the light source include metal halide lamp, mercury arc lamp, xenon arc lamp, fluorescent lamp, carbon arc lamp, tungsten-halogen duplicate lamp and sunlight.

[0074]

The irradiation conditions in the polymerization (curing) under irradiation of an active energy ray may be appropriately selected according to the light transmission which varies depending on the film thickness of the polymerizable composition (the object to be cured) or the blending of a pigment or the like. In the case of curing a paint film having a thickness of about 20 μm by irradiating an ultraviolet ray, the dose may be from 1 to 2,000 mJ/cm^2 ,

preferably from 10 to 1,000 mJ/cm². Furthermore, when the object to be cured contains a solvent, light can be irradiated after removing the solvent by heating or the like.

[0075]

In the case of polymerization (curing) under heat, the conditions are generally a temperature of approximately from 50 to 400°C and a curing time of 5 seconds to 60 minutes, preferably approximately from 80 to 250°C and from 10 seconds to 30 minutes.

[0076]

After the irradiation of an active energy ray, if desired, the cured material may be heated. By this after-heating, the unreacted material remaining in the cured material may be reduced and the cure distortion generated in the cured material due to irradiation of an active energy ray may be relaxed. As a result, the cured material can be improved in the hardness and in the case of a paint film, adhesion to the substrate as adherend can be improved. This after-heating can be generally performed in an atmosphere temperature of 80 to 300°C for 5 seconds to 30 minutes.

[0077]

The polymerizable composition of the present invention can be applied to substrates such as metal, rubber, plastic,

paper, wood, glass, ceramic and concrete.

[0078]

Examples of the use of the photosensitive resin composition of the present invention include a coating material, an adhesive, a sealing agent, a construction and building material, a stacked plate, other electrical and electric parts, a photoresist, a solder resist, a layer insulating material for multilayer circuit boards, the repair of concrete structures, a material for cast molding, a printing ink, a sealant, and a material for stereolithography.

[0079]

[Examples]

The present invention is described in greater detail below by referring to the Examples and the Comparative Examples, however, the present invention should not be construed as being limited to these Examples. Unless otherwise indicated, the term "parts" used in Examples and Comparative Examples is "parts by mass".

[0080]

Among the materials used in the Examples and the Comparative Examples, the commercially available products are shown below and these were used in their original condition without passing through any purification.

[0081]

EPIKOTE 828: bisphenol A-type epoxy resin, produced by Yuka Shell Epoxy K.K.; XDO: 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene, produced by Toa Gosei; EPIKOTE 152: phenol-novolak type epoxy resin, produced by Yuka Shell Epoxy K.K.; KRM-2110: alicyclic base resin, produced by Asahi Denka Kogyo K.K.; SUN-AID SI-60L: SbF_6^- type sulfonium salt cationic polymerization initiator, produced by Sanshin Kagaku Kogyo; UVI-6990: triaryl sulfonium hexafluorophosphate salt-type cationic polymerization initiator, produced by UCC.

[0082]

The compounds used, which are not available on the market, were chemically synthesized by the present inventors.

[0083]

Method for Evaluating Polymerizability and Physical Properties of Cured Material:

In the evaluation of polymerizability and physical properties of cured material, the reaction conversion, the surface hardness and the pencil scratch value of cured material were determined and used as an index. Specifically, the values were determined by the following operations.

[0084]

1) Reaction Conversion

The reaction conversion was calculated from the variation of infrared absorption spectrum before and after the polymerization of the polymerizable composition coated on a silicon wafer to a thickness of 10 μm .

[0085]

The infrared absorption spectrum was measured by the transmission method using an FTIR measuring apparatus (Fourier transformation infrared spectrophotometer, Model VALOR-III, manufactured by Nihon Bunko K.K.).

[0086]

The reaction conversion was determined according to the following formula from the variation in absorbance of the characteristic absorption peak before and after the irradiation in the measurement of infrared absorption spectrum, more specifically, at 980 cm^{-1} as the characteristic absorption of oxetanyl group, at from 789 to 798 cm^{-1} as the characteristic absorption of alicyclic epoxy group, and at 773 cm^{-1} as the characteristic absorption of glycidyl group.

[0087]

Conversion =

$$(1 - \text{absorbance of characteristic absorption peak after irradiation}) / \text{absorbance of characteristic}$$

absorption peak before irradiation) × 100 (%)

In Examples 6 to 8, the average of reaction conversion values of oxetanyl group and epoxy group present within the same molecule was used as the conversion. In Comparative Examples 3 to 8, the conversion was calculated from the peak of characteristic absorption (glycidyl group in EPIKOTE 828, oxetanyl group in XDO, and alicyclic epoxy group in KRM-2110) of the material used for comparison.

[0088]

2) Surface Hardness

The surface hardness of cured material was measured using a hard hardness tester manufactured by Colman Co. (GYZJ934-1). The measurement temperature was 23°C.

[0089]

3) Pencil Scratch Value of Cured Material

The cured film of polymerizable composition on a silicon wafer was measured in accordance with JIS K5400.

[0090]

Thermopolymerization of Composition:

[0091]

(Example 1)

To 100 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spiro-nonane, 5 parts of an acid generation-type cationic polymerization initiator "SUN-AID SI-60, produced by Sanshin Kagaku Kogyo K.K." was added and thoroughly stirred

to obtain a thermopolymerizable composition. A 2 mm-thick rubber spacer bored to a diameter of 5 cm was placed on a 2 mm-thick glass plate, the thermopolymerizable composition was poured into the bored hole, and another glass plate was fixed thereto not to allow the entering of air. Two units of this device were prepared and left standing in an oven at 120°C. One was taken out from the oven after the passing of 10 minutes and another was taken out after the passing of 30 minutes to obtain cured materials having a diameter of 5 cm and a thickness of 2 mm. When the cured materials returned to room temperature, the temperature was adjusted to 23°C and the surface hardness of each cured material with a curing time of 10 minutes or 30 minutes was measured. The results obtained are shown in Table 1.

[0092]

(Example 2)

The operation was performed thoroughly in the same manner as in Example 1 except for using 6,7-epoxy-2-oxa-[3.5]spirononane in place of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane of Example 1, and the surface hardness of each cured material was measured. The results obtained are shown in Table 1.

[0093]

(Example 3)

The operation was performed thoroughly in the same

manner as in Example 1 except for using spiro[5,6-epoxynorbornane-2,3'-oxetane] in place of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane of Example 1, and the surface hardness of each cured material was measured. The results obtained are shown in Table 1.

[0094]

(Example 4)

The operation was performed thoroughly in the same manner as in Example 1 except for using a mixture of 90 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane and 10 parts of EPIKOTE 828 (produced by Yuka Shell Epoxy K.K.) in place of 100 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane of Example 1, and the surface hardness of each cured material was measured. The results obtained are shown in Table 1.

[0095]

(Example 5)

The operation was performed thoroughly in the same manner as in Example 1 except for using a mixture of 80 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane, 10 parts of EPIKOTE 828 (produced by Yuka Shell Epoxy K.K.) and 10 parts of 5-methyl-2-oxaspiro[3.5]nonane in place of 100 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane of Example 1, and the surface hardness of each cured material was measured. The results obtained are shown in Table 1.

[0096]

(Example 6)

The operation was performed thoroughly in the same manner as in Example 1 except for using a mixture of 10 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane and 90 parts of EPIKOTE 152 (produced by Yuka Shell Epoxy K.K.) in place of 100 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane of Example 1, and the surface hardness of each cured material was measured. The results obtained are shown in Table 1.

[0097]

(Comparative Examples 1 and 2)

The operations were performed thoroughly in the same manner as in Example 1 except for using a heat polymerizable composition having constituent components shown in Table 1, and the surface hardness of each cured material was measured. The results obtained are shown in Table 1.

[0098]

As is apparent from Table 1, the polymerizable compositions of the present invention in Examples 1 to 5 reached the final hardness by the heating for about 10 minutes and this reveals that the compositions each is quickly polymerized and cured.

[0099]

Also, it is seen from the comparison between Example 6 and Comparative Example 2 that the curing rate of epoxy resin can be improved by blending about 10 parts by mass of the alicyclic alkane (a) having an oxetanyl group and an epoxy group within the molecule of the present invention, with the epoxy resin.

[0100]

[Table 1]

Blending of Polymerizable Composition and Surface Hardness of Cured Material

Name of Compound	Examples						Comparative Examples	
	1	2	3	4	5	6	1	2
7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane	100	0	0	90	80	10	0	0
6,7-epoxy-2-oxa-[3.5]spiro-nonane	0	100	0	0	0	0	0	0
Spiro[5,6-epoxynorbornane-2,3'-oxetane]	0	0	100	0	0	0	0	0
5-Methyl-2-oxaspiro[3.5]-nonane	0	0	0	0	10	0	0	0
EPIKOTE 828	0	0	0	10	10	0	0	0
XDO	0	0	0	0	0	0	100	0
EPIKOTE 152	0	0	0	0	0	90	0	100
SUN-AID SI-60	5	5	5	5	5	5	5	5
Surface hardness (hard) after heat-curing for 10 minutes	20	18	22	20	18	20	0	5
after heat-curing for 30 minutes	25	24	27	25	24	25	2	10

[0101]

Photopolymerization of Composition

[0102]

(Example 7)

To 100 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spiro-nonane, 5 parts of photoacid generation-type cationic polymerization initiator "UVI-6990" produced by Union Carbide K.K. was added and thoroughly stirred to obtain a photopolymerizable composition.

[0103]

Subsequently, this composition was coated on a silicon wafer to a thickness of 10 μm and the conversion of reactive groups was determined at the time of irradiating a high-pressure mercury lamp at 1.45 mW/cm^2 for 10 seconds or for 30 seconds.

[0104]

Furthermore, in accordance with the measurement method of 3) Pencil Scratch Value above, the pencil scratch value of the cured film on the silicon wafer obtained by the irradiation for 30 seconds was measured. The results obtained are shown together in Table 2.

[0105]

(Example 8)

The operation was performed thoroughly in the same manner as in Example 7 except for using a mixture of 90

parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane and 10 parts of EPIKOTE 828 (produced by Yuka Shell Epoxy K.K.) in place of 100 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane of Example 7, and the conversion and the pencil scratch value were measured. The results obtained are shown in Table 2.

[0106]

(Example 9)

The operation was performed thoroughly in the same manner as in Example 7 except for using a mixture of 50 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane and 50 parts of EPIKOTE 828 (produced by Yuka Shell Epoxy K.K.) in place of 100 parts of 7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane of Example 7, and the conversion and the pencil scratch value were measured. The results obtained are shown in Table 2.

[0107]

From the results of Examples 7 to 9, it was verified that the conversion of oxetanyl group and alicyclic epoxy group was more improved and the curing rate is more elevated by blending an epoxy compound as a constituent element of the composition of the present invention with the alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule.

[0108]

(Comparative Examples 3 to 5)

The operation was performed thoroughly in the same manner as in Example 7 except for using a photo-polymerizable composition having constituent elements shown in Table 2, and the conversion and the pencil scratch value were measured. The results obtained are shown in Table 2.

[0109]

As is apparent from Table 2, the polymerizable compositions of the present invention in Examples 7 to 9 were quickly decreased in the reactive groups, namely, quickly polymerized, after the light irradiation as compared with Comparative Examples 3 to 5, revealing that the compositions can be polymerized and cured within a short period of time.

[0110]

[Table 2]

Blending and Conversion of Polymerizable Composition and
Pencil Scratch Value of Cured Material

Name of Compound	Examples			Comparative Examples		
	7	8	9	3	4	5
7,8-epoxy-2-oxa-5-methyl-[3.5]spirononane	100	90	50	0	0	0
EPIKOTE 828	0	10	50	0	0	0
XDO	0	0	0	100	0	0
EPIKOTE 152	0	0	0	0	100	0
KRM-2110	0	0	0	0	0	100
UVI-6990	5	5	5	5	5	5
Conversion (%) after irradiation of 10 seconds	63	70	87	20	24	13
after irradiation of 30 seconds	82	83	91	46	40	29
Pencil scratch value	3H	3H	3H	3H	3H	3H

[0111]

In the Examples and Comparative Examples of each Table,
compounds shown below were used.

EPIKOTE 828: bisphenol A-type epoxy resin, produced by
Yuka Shell Epoxy K.K.

XDO: 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]-
benzene, produced by Toa Gosei

EPIKOTE 152: phenol novolak type epoxy resin, produced
by Yuka Shell Epoxy K.K.

KRM-2110: alicyclic base resin, produced by Asahi

Denka Kogyo K.K.

SUN-AID SI-60L: SbF_6^- type sulfonium salt cationic polymerization initiator, produced by Sanshin Kagaku Kogyo K.K.

UVI-6990: triaryl sulfonium hexafluorophosphate salt-type cationic polymerization initiator, produced by UCC.

[0112]

[Effects of the Invention]

The present invention provides a cationic polymerizable composition exhibiting high activity (quick curability) under heat and/or under irradiation of an active energy ray and also provides a cured material thereof and a method for producing the cured material. The present invention can be applied to the coating on paper or plastic having poor heat resistance and further can be applied to a paint, an adhesive, a sealing agent, a construction and building material, a stacked plate, other electrical and electronic parts, a photoresist, a solder resist, a layer insulating film for multilayer circuit boards, the repair of concrete structures, a material for cast molding, a printing ink, a sealant, and a material for stereolithography.

[NAME OF DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a cationic polymerizable composition exhibiting high activity (quick polymerizability, quick curability) under irradiation of an active energy ray and/or under heat.

[MEANS TO SOLVE THE PROBLEM]

It is found that a polymerizable composition comprising (a) an alicyclic alkane having an oxetanyl group and an epoxy group within the same molecule and (b) a compound capable of initiating cationic polymerization under irradiation of an active energy ray and/or under heat exhibits high activity in the photo- or heat-cationic ring-opening polymerization and that the polymerization product thereof (cured material) has good properties.

[SELECTED DRAWING] None.